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<b>(54) Title:</b> PERFLUOROELASTOMER COMPOSITIONS  <b>(57) Abstract</b>  A perfluoroelastomer compound having improved processability comprising a perfluoroolefin, a perfluorovinyl ether and a halogen-containing cure site, where the polymer contains substantially no ionizable moieties; and processes for making such copolymers; and articles made therefrom.		

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## PERFLUOROELASTOMER COMPOSITIONS

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### FIELD OF THE INVENTION

This invention relates to peroxide-curable perfluoroelastomer compositions which have excellent processability, and which when cured, have excellent physical properties.

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### BACKGROUND OF THE INVENTION

Perfluoroelastomers (elastomeric perfluoropolymers) are polymeric materials which exhibit outstanding high temperature tolerance and chemical resistance. Consequently, such compositions are particularly adapted for use as seals and gaskets in systems in which elevated temperatures and/or corrosive chemicals are encountered. They are useful in industries such as, chemical processing, semiconductor, aerospace, petroleum, etc.

The outstanding properties of perfluoropolymers are largely attributable to the stability and inertness of the copolymerized perfluorinated monomer units which make up the major portion of the polymer backbone, e.g., tetrafluoroethylene and perfluoro(alkyl vinyl) ethers. In order to completely develop elastomeric properties, perfluoropolymers are typically crosslinked, i.e. vulcanized. To this end, a small percentage of a cure site monomer is copolymerized with the perfluorinated monomer units. Cure site monomers containing at least one bromo or iodo group are known. Such cure site monomers, when combined with a peroxide and a coagent, will provide a suitably cured composition.

Perfluoroelastomers are very expensive materials, and therefore are only used in situations where no other material will do the job. In view of the very high raw material costs, scrap rates during the molding operation must be kept to a minimum. Unfortunately, perfluoroelastomers are known to be very difficult to process with respect to compounding, flow characteristics and mold release. When conventional initiators are used to produce the polymers (e.g., persulfates) the polymeric end groups are typically of an ionic and/or acidic nature. These ionizable polymer end-groups, that are normally present, are prone to undesirable reactions with some commonly used additives, (e.g., acid

acceptors). Examples of commonly used acid acceptors are zinc oxide, calcium hydroxide, calcium carbonate, magnesium oxide, etc. They are used in the compound formulation to bind any HF or other acids that might be generated at the high temperatures where perfluoroelastomers must function.

5 Perfluoroelastomer compounds that show very good processing characteristics are much desired. Because many applications for these polymers also require good sealing capabilities, the steps to improve processability are preferably not detrimental to critical physical properties such as compression set resistance.

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## SUMMARY OF THE INVENTION

The perfluoroelastomers compounds of this invention employ a perfluoroelastomer that is prepared using an initiator combination of an oxidizer and a perfluoroalkyl sulfinate of type  $R_fSO_2Na$ . The copolymers prepared in this manner surprisingly can be processed  
15 like other elastomer gums. They are easy to process on conventional 2 roll mills, or mixing devices, i.e. the mills or mixing devices need not be heated above room temperature. Their compound viscosity does not increase when acid acceptors, such as  $Ca(OH)_2$ , are added. The perfluoroelastomers also show improved physical properties (e.g. compression set resistance).

20 One embodiment of the invention provides a peroxide curable perfluoroelastomer compound that is easily processable and is essentially free of ionizable end groups. By "essentially free" of such groups it is meant that less than 10% of these end groups are ionizable groups. The compound of this embodiment comprises:

25 A) a perfluoroelastomer containing interpolymerized units derived from 1) a perfluoroolefin, 2) a perfluorovinyl ether selected from the group consisting of perfluoro(alkyl vinyl) ethers, perfluoro(alkoxy vinyl) ethers, and mixtures thereof, and 3) a cure site component containing a halogen group capable of participation in a peroxide cure reaction, selected from the group consisting of fluorinated olefins having at least one such halogen group,  
30 fluorinated vinyl ethers having at least one such halogen group, chain transfer agents containing at least one such halogen group, and initiators containing at least one such halogen group, and mixtures thereof; with the

proviso that the cure site component contains substantially no nitrile groups, and

B) a peroxide curative.

In another embodiment, the invention provides a peroxide curable

5 perfluoroelastomer compound that is easily processable comprising:

A) a perfluoroelastomer substantially free of ionizable end groups, wherein the perfluoroelastomer contains interpolymerized units derived from 1) a perfluoroolefin, 2) a perfluorovinyl ether selected from the group consisting of perfluoro(alkyl vinyl) ethers, perfluoro(alkoxy vinyl) ethers, and mixtures thereof, and 3) a cure site component containing a bromine or iodine atom capable of participation in a peroxide cure reaction, selected from the group consisting of brominated or iodinated olefins having at least one such atom, brominated or iodinated vinyl ethers having at least one such atom, brominated or iodinated chain transfer agents, brominated or iodinated initiators, and mixtures thereof, and

B) a peroxide curative.

The present invention also provides a method for improving the processability of perfluoroelastomers, comprising: polymerizing, under free-radical conditions, an aqueous emulsion or suspension of a polymerizable mixture comprising a perfluoroolefin and a perfluoroalkyl vinyl ether or a perfluoroalkoxy vinyl ether and mixtures thereof, a halogen-containing cure-site component capable of participation in a peroxide cure reaction, a fluoroaliphatic-radical containing sulfinate, and an oxidizing agent capable of oxidizing said sulfinate to a sulfonyl radical, with the proviso that the cure site component contains substantially no nitrile groups.

25 The present invention also provides a method for improving the processability of perfluoroelastomers, comprising: polymerizing, under free-radical conditions, an aqueous emulsion or suspension of a polymerizable mixture comprising a perfluoroolefin and a perfluoroalkyl vinyl ether or a perfluoroalkoxy vinyl ether and mixtures thereof, a bromine- or iodine-containing cure-site component, a fluoroaliphatic-radical containing sulfinate, and an oxidizing agent capable of oxidizing said sulfinate to a sulfonyl radical.

30 The invention further relates to cured and uncured articles made from such curable compounds.

## DETAILED DESCRIPTION

The compositions of the present invention comprise peroxide curable  
 5 perfluoroelastomers which are characterized by improved processability and less reactivity  
 to bases. These compositions comprise a) a perfluoroelastomer having copolymerized  
 units of a perfluoroolefin, a perfluorovinyl ether and a cure site component having at least  
 one bromine- or iodine-containing moiety, and b) a compound which acts as a curative for  
 the perfluoroelastomer. The perfluoroelastomers are substantially free of ionizable end  
 10 groups, such as those reactive with bases. This does not preclude the presence of cure  
 sites in the perfluoroelastomers needed for crosslinking.

Examples of suitable perfluorinated olefins useful in the invention include  
 tetrafluoroethylene and hexafluoropropylene.

Examples of suitable perfluorinated vinyl ethers are those of the formula  
 15 
$$\text{CF}_2=\text{CFO}(\text{R}_f\text{O})_n(\text{R}'_f\text{O})_m\text{R}_f \quad (\text{I})$$

where  $\text{R}_f$  and  $\text{R}'_f$  are different linear or branched perfluoroalkylene groups of 2-6 carbon  
 atoms,  $m$  and  $n$  are independently 0-10, and  $\text{R}_f$  is a perfluoroalkyl group of 1-6 carbon  
 atoms.

A preferred class of perfluoro(alkyl vinyl) ethers includes compositions of the  
 20 formula 
$$\text{CF}_2=\text{CFO}(\text{CF}_2\text{CFXO})_n\text{R}_f \quad (\text{II})$$

where  $\text{X}$  is  $\text{F}$  or  $\text{CF}_3$ ,  $n$  is 0-5, and  $\text{R}_f$  is a perfluoroalkyl group of 1-6 carbon atoms.

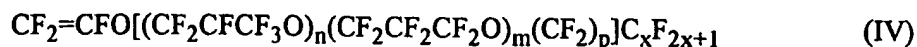
Most preferred perfluoro(alkyl vinyl) ethers are those wherein  $n$  is 0 or 1 and  $\text{R}_f$   
 contains 1-3 carbon atoms. Examples of such perfluorinated ethers include  
 perfluoro(methyl vinyl) ether, perfluoro(ethyl vinyl) ether, and perfluoro(propyl vinyl)  
 25 ether. Other useful monomers include compounds of the formula



where  $\text{R}_f$  is a perfluoroalkyl group having 1-6 carbon atoms,  $m=0$  or 1,  $n=0-5$ , and  $\text{Z}=\text{F}$  or  
 $\text{CF}_3$ .

Preferred members of this class are those in which  $\text{R}_f$  is  $\text{C}_3\text{F}_7$ ,  $m=0$ , and  $n=1$ .

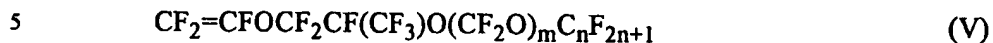
30 Additional perfluoro(alkyl vinyl) ether monomers useful in the invention include  
 compounds of the formula



where  $m$  and  $n=1-10$ ,  $p=0-3$ , and  $x=1-5$ .

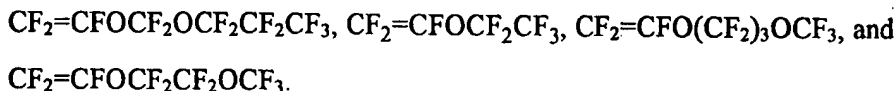
Preferred members of this class include compounds where  $n=0-1$ ,  $m=0-1$ , and  $x=1$ .

Examples of perfluoro(alkoxy vinyl) ethers useful in the invention include



where  $n=1-5$ ,  $m=1-3$ , and where, preferably,  $n=1$ .

Specific examples of useful perfluorovinyl ethers useful in the invention include



Mixtures of perfluoro(alkyl vinyl) ethers and perfluoro(alkoxy vinyl) ethers may also be used.

Preferred copolymers are composed of tetrafluoroethylene and at least one perfluoro(alkyl vinyl) ether as principal monomer units. In such copolymers, the copolymerized perfluorinated ether units constitute from about 15-50 mole percent of total monomer units in the polymer.

The cure site component used in the present invention is a halogen containing material that is capable of participation in a peroxide cure reaction. Typically the halogen is bromine or iodine. Suitable cure-site components include terminally unsaturated monoolefins of 2 to 4 carbon atoms such as bromodifluoroethylene, bromotrifluoroethylene, iodotrifluoroethylene, and 4-bromo-3,3,4,4-tetrafluorobutene-1. Examples of other suitable cure site components include  $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{Br}$ ,  $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CF}_2\text{Br}$ , and  $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{Br}$ . Preferably, all or essentially all of these components are ethylenically unsaturated monomers.

Other useful cure-site components are brominated or iodinated chain transfer agents and initiators. Examples of useful chain transfer agents include perfluoroalkyl bromides or iodides. Examples of useful initiators include  $\text{NaO}_2\text{SC}_2\text{F}_4\text{OF}_4\text{X}$  (where  $\text{X}$  is  $\text{Br}$  or  $\text{I}$ ).

Suitable peroxide curatives for use in the invention are those which generate free radicals at curing temperatures. A dialkyl peroxide or a bis(dialkyl peroxide) which decomposes at a temperature above  $50^\circ\text{C}$  is especially preferred. In many cases it is preferred to use a di-tertiarybutyl peroxide having a tertiary carbon atom attached to

peroxy oxygen. Among the most useful peroxides of this type are 2,5-dimethyl-2,5-di(tertiarybutylperoxy)hexyne-3 and 2,5-dimethyl-2,5-di(tertiarybutylperoxy)hexane. Other peroxides can be selected from such compounds as dicumyl peroxide, dibenzoyl peroxide, tertiarybutyl

5 perbenzoate,  $\alpha,\alpha'$ -bis(t-butylperoxy-diisopropylbenzene), and di[1,3-dimethyl-3-(t-butylperoxy)-butyl]carbonate. Generally, about 1-3 parts of peroxide per 100 parts of perfluoroelastomer is used.

Another material which is usually blended with the composition as a part of the curative system is a coagent composed of a polyunsaturated compound which is capable of

10 cooperating with the peroxide to provide a useful cure. These coagents can be added in an amount equal to 0.1 and 10 parts per hundred parts perfluoroelastomer, preferably between 2-5 parts per hundred parts perfluoroelastomer. Examples of useful coagents include triallyl cyanurate; triallyl isocyanurate; tri(methylallyl isocyanurate); tris(diallylamine)-s-triazine; triallyl phosphite; N,N-diallyl acrylamide; hexaallyl phosphoramidate; N,N,N',N'-

15 tetraalkyl tetraphthalamide; N,N,N',N'- tetraallyl malonamide; trivinyl isocyanurate; 2,4,6-trivinyl methyltrisiloxane; and tri(5-norbornene-2-methylene)cyanurate. Particularly useful is triallyl isocyanurate.

Other useful coagents include the bis-olefins disclosed in EPA 0 661 304 A1, EPA 0 784 064 A1 and EPA 0 769 521 A1.

20 Additives, such as carbon black, stabilizers, plasticizers, lubricants, fillers, and processing aids typically utilized in perfluoroelastomer compounding can be incorporated into the compositions of the present invention, provided they have adequate stability for the intended service conditions. In particular, low temperature performance can be enhanced by incorporation of perfluoropolyethers (cf. U.S. Pat No. 5,268,405).

25 Carbon black fillers are used in elastomers as a means to balance modulus, tensile strength, elongation, hardness, abrasion resistance, conductivity, and processability of the compositions. Suitable examples include MT blacks (medium thermal black) designated N-991, N-990, N-908, and N-907, and large particle size furnace blacks. When used, 1-70 phr of large size particle black is generally sufficient.

30 In addition, fluoropolymer fillers may also be present in the composition. Generally, from 1 to 50 parts per hundred perfluoroelastomer of a fluoropolymer filler is used. The fluoropolymer filler can be finely divided, easily dispersed plastic



fluoropolymer that is solid at the highest temperature utilized in fabrication and curing of the perfluoroelastomer composition. By solid, it is meant that the fluoroplastic, if partially crystalline, will have a crystalline melting temperature above the processing temperature(s) of the perfluoroelastomer(s). Such finely divided, easily dispersed fluoroplastics are commonly called micropowders or fluoroadditives. Micropowders are ordinarily partially crystalline polymers.

The method of this invention comprises the use of perfluorosulfinate and an oxidizing agent in a free-radical polymerization process. The polymerization process includes free-radical polymerization of monomers alone or as solutions, emulsions, or dispersions in an organic solvent or water. Polymerization in an aqueous emulsion or suspension is often preferred because of the rapid and nearly complete conversion of monomers, easy removal of the heat of polymerization, and ready isolation of the polymer. Emulsion or suspension polymerization typically involves polymerizing monomers in an aqueous medium in the presence of an inorganic free-radical initiator system and surfactant or suspending agent.

Aqueous emulsion polymerization can be carried out continuously under steady-state conditions in which, for example, monomers, water, surfactants, buffers and catalysts are fed continuously to a stirred reactor under optimum pressure and temperature conditions while the resulting emulsion or suspension is removed continuously. An alternative technique is batch or semibatch polymerization by feeding the ingredients into a stirred reactor and allowing them to react at a set temperature for a specified length of time or by charging ingredients into the reactor and feeding the monomer into the reactor to maintain a constant pressure until a desired amount of polymer is formed.

A class of the fluoroaliphatic sulfinates useful in this invention are found in U.S. patent No. 5,285,002 incorporated herein by reference and can be represented by the following general formulae



or



wherein  $R^3_f$  represents a monovalent fluoroaliphatic radical having, for example, from 1 to 20 carbon atoms, preferably 4 to 10 carbon atoms,  $R^2_f$  represents a polyvalent, preferably

divalent, fluoroaliphatic radical having, for example, from 1 to 20 carbon atoms, preferably from 2 to 10 carbon atoms, M represents a hydrogen atom or cation with valence x, which is 1 to 2, and is preferably 1, and n is 1 to 4, preferably 1 or 2.

The monovalent fluoroaliphatic radical,  $R^3_f$  is a fluorinated, stable, inert, non-polar, saturated moiety. It can be straight chain, branched chain, and, if sufficiently large, cyclic, or combinations thereof, such as alkyl cycloaliphatic radicals. Generally,  $R^3_f$  will have 1 to 20 carbon atoms, preferably 4 to 10, and will contain 40 to 83 weight percent, preferably 50 to 78 weight percent fluorine. The preferred compounds are those in which the  $R^3_f$  group is fully or substantially completely fluorinated, as in the case where  $R^3_f$  is perfluoroalkyl,  $C_nF_{2n+1}$ , where n is 1 to 20.

The polyvalent, preferably divalent, fluoroaliphatic radical,  $R^2_f$  is a fluorinated, stable, inert, non-polar, saturated moiety. It can be straight chain, branched chain, and, if sufficiently large, cyclic or combinations thereof, such as alkylcycloaliphatic diradicals. Generally,  $R^2_f$  will have 1 to 20 carbon atoms, preferably 2 to 10. The preferred compounds are those in which the  $R^2_f$  group is perfluoroalkylene,  $C_nF_{2n}$ , where n is 1 to 20, or perfluorocycloalkyl,  $C_nF_{2n}$ , where n is 5 to 20.

With respect to either  $R^3_f$  or  $R^2_f$  the skeletal chain of carbon atoms can be interrupted by divalent oxygen, hexavalent sulfur or trivalent nitrogen hetero atoms, each of which is bonded only to carbon atoms, but preferably where such hetero atoms are present, such skeletal chain does not contain more than one said hetero atom for every two carbon atoms. An occasional carbon-bonded hydrogen atom, iodine, bromine, or chlorine atom may be present; where present, however, they preferably are present not more than one for every two carbon atoms in the chain. Where  $R^3_f$  or  $R^2_f$  is or contains a cyclic structure, such structure preferably has 6 ring member atoms, 1 or 2 of which can be said hetero atoms, e.g., oxygen and/or nitrogen. Examples of  $R^3_f$  radicals are fluorinated alkyl, e.g.,  $C_4F_9$ -,  $C_6F_{13}$ -,  $C_8F_{17}$ -, alkoxyalkyl, e.g.,  $C_3F_7OCF_2$ -. Examples of  $R^2_f$  are fluorinated alkylene, e.g.,  $-C_4F_8-$ ,  $-C_8F_{16}-$ . Where  $R^3_f$  is designated as a specific radical, e.g.,  $C_8F_{17}$ -, it should be understood that this radical can represent an average

structure of a mixture, e.g.,  $C_6F_{13}$ -- to  $C_{10}F_{21}$ --, which mixture can also include branched structures.

Representative fluoroaliphatic sulfinate compounds useful in the method of this invention include the following:

- 5  $CF_3SO_2Na$   
 $C_4F_9SO_2H$   
 $C_8F_{17}SO_2Na$   
 $CF_3C(Cl)_2CF_2SO_2K$   
 $Cl(CF_2)_8OC_2F_4SO_2Na$   
10  $Cl(CF_2)_xCF_2SO_2Na$ , where x is 0, 1, 3, 4, 7, 9  
 $NaO_2SC_8F_{16}SO_2Na$   
 $NaO_2SC_6F_{12}SO_2Na$   
 $NaO_2SC_2F_4OC_2F_4SO_2Na$   
 $NaO_2SC_2F_4OC_2F_4X$ , where X is Br or I  
15  $NaO_2S[C_4F_8O]_nC_3F_6SO_2Na$   
 $NaO_2SCF_2O(CF_2CF_2O)_m(CF_2O)_nCF_2SO_2Na$   
 $(CF_3)_2NCF_2CF_2SO_2Na$   
 $(C_2F_5)_2NCF_2CF_2SO_2Na$   
 $N(C_2F_4SO_2Na)_3$   
20  $NaO_2SC_8F_{16}SO_2F$   
 $NaO_2SCF_2CF_2-N \begin{array}{c} \diagup \quad \diagdown \\ F \end{array} N-CF_2CF_2SO_2Na$   
 $\begin{array}{c} \diagup \quad \diagdown \\ Q \quad F \quad N \end{array} - CF_2CF_2SO_2Na$   
 $NaO_2SC_3F_6O(C_4F_8O)_nC_3F_6SO_2Na$  where n is 4 to 8.

- Combinations of monosulfates, disulfates, and trisulfates can be used,  
25 depending on whether it is desired to use sulfinate as an initiator, a monomer, or both. When polyvalent sulfates, such as those represented by Formula VII, are used, the sulfinate is a monomer and the fluorinated moiety is incorporated into the polymer backbone. When monosulfates are used the fluorinated moiety is incorporated as a polymer end group.

The amount of fluoroaliphatic sulfinates used in the method(s) of the invention can vary, depending, for example, on the molecular weight of polymer desired. Preferably the amount of fluoroaliphatic sulfinate is from 0.01 to 50 mole %, and most preferably from 0.05 to 10 mole %, of sulfinate compound based on total quantity of monomers.

5 In addition to the sulfinate, other reducing agents can be present, such as sodium, potassium or ammonium sulfites, bisulfite, metabisulfite, hyposulfite, thiosulfite, phosphite, sodium or potassium formaldehyde sulfoxylate or hypophosphite. Activators such as ferrous, cuprous, and silver salts, may also be present.

The oxidizing agent used in the method of the invention is water soluble and is  
10 capable of converting the sulfinate to a sulfonyl moiety. The sulfonyl radical produced in the method of the invention is believed to eliminate SO<sub>2</sub> and form a fluorinated radical that initiates the polymerization of the ethylenically unsaturated monomers.

A number of useful oxidizing agents are known as taught in U.S. Patent 5,285,002. Representative examples of such useful oxidizing agents are sodium, potassium, and  
15 ammonium persulfates, perphosphates, perborates, percarbonates, bromates, chlorates and hypochlorites. Other useful oxidizing agents include cerium IV compounds such as (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub>. It is understood that this list of oxidizing agents is exemplary only. One of ordinary skill in the art will recognize that there are other oxidizing agents useful in the invention based upon this disclosure.

20 The amount of oxidizing agent used can vary depending on the particular oxidizing agent and sulfinate employed. Typically an equimolar amount or less (based on the amount of sulfinate) is used.

The curable compositions of the present invention may be prepared by mixing a perfluoroelastomer, a peroxide curative, and other additives in conventional rubber  
25 processing equipment. Such equipment includes rubber mills, internal mixers, such as Banbury mixers, and mixing extruders.

Prior to the present invention, it was difficult to prepare compositions containing perfluoroelastomer. Typically the compositions required the use of heated processing equipment to keep the compositions from forming crumbly masses. The  
30 perfluoroelastomer compounds of this invention do not require the use of heated rolls or processing equipment during compounding. They can be prepared at ambient temperatures without forming a crumbly mass. The substantial lack of reactive end groups

on the perfluoroelastomers is at least partially responsible for this. The substantial lack of these groups minimizes reactive problems, such as exotherm or significant viscosity increase during addition of acid acceptors. The lack of compound viscosity increase prevents problems with flow and filling of mold cavities. The ability to compound at lower temperatures minimizes the problem of premature onset of the cure or crosslinking reaction.

The curable compositions of the present invention are useful in production of articles such as gaskets, tubing, and seals. Such articles are produced by molding a compounded formulation of the curable composition with various additives under pressure, curing the part, and then subjecting it to a post cure cycle. During the molding step, the perfluoroelastomers of the invention demonstrate an additional advantage. Lower viscosity is evidenced by faster mold filling or the lower pressures required. Improved mold release is apparent when removing the press cured part or injection molded part from the mold. The cured compositions have excellent thermal stability and chemical resistance. They are particularly useful in applications such as seals and gaskets for manufacturing semiconductor devices, and in seals for high temperature automotive uses.

The following examples will further demonstrate the present invention. In these examples, the properties were tested as follows.

Mooney viscosity was determined by ASTM D 1646-96 (ML 1+10@121°C).

Results are reported in Mooney units.

Cure Rheology Tests were run on compounded admixtures using a Monsanto Moving Die Rheometer (MDR) Model 2000 in accordance with ASTM D 5289-95 at 177°C, no preheat, 12 minute elapsed time (unless otherwise specified) and a 0.5° arc. Values were obtained for Minimum torque (ML), Maximum torque (MH), i.e., highest torque attained during specified period of time when no plateau or maximum was obtained, were measured. Also reported were:  $t_{s2}$  (time for torque to increase 2 units above ML),  $t'_{50}$  (time for torque to reach  $ML + 0.5[MH-ML]$ ), and  $t'_{90}$  (time for torque to reach  $ML + 0.9[MH-ML]$ ). Torque is reported as deci Newton meters (dNm).

Press-cured samples (150 x 150 x 2.0 mm sheets, unless otherwise noted) were prepared for physical property determination by pressing at about 6.9 MegaPascals (MPa) for the indicated amount of time and temperature.

Post-cured samples were prepared by placing a press-cured sample in a circulating air oven. The oven was maintained at the indicated temperatures and the samples treated for the indicated amount of time.

Force per unit area is reported as Mega Pascals (MPa).

5 Physical properties were obtained according to ASTM D-412 and Hardness was obtained according to ASTM D 2240.

Compression sets were determined by ASTM D 395-89 Method B with 0.139 inch (3.5 mm) O-rings compressed for 70 hours at 200°C. Results are reported as %.

10

### EXAMPLE 1

Several fluoropolymers were prepared in a manner similar to Example 1 of U.S. Patent No. 5,285,002 except the monomers and other ingredients used are as listed below in gram weight quantities. The monomers used were tetrafluoroethylene (TFE), perfluoromethyl vinyl ether (PMVE) and bromotrifluoroethylene (BTFE).  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  was identified as APS. The fluorochemical sulfinate ( $\text{C}_4\text{F}_9\text{SO}_2\text{Na}$ ) was prepared as discussed in U.S. Patent No. 5,285,002.

	Comparative Polymer A	Polymer A
Deionized (DI) water:	2,777	2,774
20 $\text{C}_7\text{F}_{15}\text{COONH}_4$ :	15.9	15.9
$\text{K}_2\text{HPO}_4$ :	10	10
$\text{C}_4\text{F}_9\text{SO}_2\text{Na}$ :	-----	4
Precharge monomers:		
TFE:	142	140
25 PMVE:	342	331
BTFE:	3.9	3
APS injected:	2	3
Runtime monomer fed:		
TFE:	662	664
30 PMVE:	496	497
BTFE:	9.7	9.9

The polymerizations were run at 60° C for 651 minutes for Comparative Polymer A and 71° C for 262 minutes for Polymer A. Both polymerizations were run at a pressure of 16 bar.

In both cases a water clear transparent polymer latex was obtained. The latex was coagulated using 30 g  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  in 1000 mL DI water. The polymers were filtered, washed several times with hot DI water and dried overnight in a circulating air oven at 100° C to form polymer gums.

The Mooney Viscosity (ML1+10 @ 121° C) of Comparative Polymer A was 76 and for Polymer A was 96.

One hundred parts by weight of each polymer gum was compounded by adding 15 parts by weight (phr) N990 carbon black, 5 phr zinc oxide, 1.5 phr Lupercos<sup>TM</sup> 101 XL organic peroxide from Atochem and 2 phr triallylisocyanate-Dry Liquid Concentrate (TAIC-DLC; 72% active), available from Harwick, to each polymer gum.

Polymer A was compounded in a conventional manner on a two-roll rubber mill. The Comparative Polymer A had to be compounded on a heated (50-70° C) two-roll mill because it was crumbly and turned powdery if it was compounded in a conventional manner (i.e., using standard or unheated conditions).

Table 1 shows the rheological data obtained from the MDR testing.

**Table 1**

20 <b>MDR (177° C)</b>	<b>Comparative Compound A</b>	<b>Compound A</b>
ML (dNm):	5.1	3.0
MH (dNm):	26	20
t <sub>g2</sub> (min.):	0.44	0.48
25 t' <sub>50</sub> (min.):	0.65	0.68
t' <sub>90</sub> (min.):	1.51	1.76

As can be seen from the MDR data, Comparative Compound A showed a significant increase in ML (a measure of compound viscosity) compared to the Compound A, even though the Mooney viscosity of Comparative Polymer A was lower than that of Polymer A. In other words, even though the raw polymer viscosity of Comparative Polymer A was lower than that of Polymer A, the addition of the fillers, acid acceptors and

curatives made the compound viscosity of Comparative Compound A rise above that of Compound A.

The data shown in Table 2 was obtained after the compounds were cured. Comparative Compound A was press cured at 150°C for 10 minutes followed by post curing for 16 hours at 150°C and further post curing for 8 hours at 200°C. Compound A was press cured at 177°C for 10 minutes followed by post curing at 200°C for 20 hours. Attempts to cure and post cure the Comparative Compound A in the same manner as Compound A failed due to warping and formation of fissures in the test sample.

Table 2

	Comparative Compound A	Compound A
Tensile Strength (MPa):	24.5	19.6
Elongation at break (%):	165	136
100% modulus (MPa):	14.1	12.7
Hardness (shoreA):	87	80
Compression set O-rings, 70 hrs@ 200 °C:	42%	30%

The compression set resistance of Compound A was significantly better than that of Comparative Compound A. Comparative Compound A also required heated rolls for compounding, a lower press cure temperature and a two-stage postcuring.

## EXAMPLE 2

These samples were made to demonstrate the reactivity of the polymer when compounding with a base or acid acceptor.

Polymer B was prepared in a manner similar to Polymer A except that no BTFE was used, 4 g of APS and 5.4 g C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>Na were used, and the polymerization was run at 11.6 bar pressure.

Comparative Polymer B was prepared in a manner similar to that of Polymer B except that no sulfinate was used, only 1 g of APS was used, and the polymerization was run at 11.0 bar pressure.

The Mooney Viscosity (ML1+10 @ 121° C) of Polymer B was 38 and Comparative Polymer B was 73.

Comparative Polymer B was milled with 15 phr MT N990 carbon black and 6 phr Ca(OH)<sub>2</sub>. The combination of ingredients started to exotherm and formed a crumbly



compound during milling. When the resulting Comparative Compound B was examined by MDR at 177° C, the torque of the crumbly compound increased from the initial 3.4 dNm to 17 dNm within 30 seconds and kept rising to 20 dNm in 10 minutes.

- Polymer B was compounded with the same additives as was Comparative
- 5 Compound B. The combination of ingredients remained as a viscous sheet on the mill and showed less than 1.1 dNm torque rise over 8 minutes on the MDR at 177° C.

- These results demonstrate the substantially lower reactivity of the compound of the invention when adding basic ingredients, such as acid acceptor. This difference is
- 10 apparent even in compounds where no cure site component is present.

**WHAT IS CLAIMED IS:**

1. A peroxide curable perfluoroelastomer compound that is easily processable comprising:
  - 5 A) a perfluoroelastomer substantially free of ionizable end groups, said perfluoroelastomer containing interpolymerized units derived from 1) a perfluoroolefin, 2) a perfluorovinyl ether selected from the group consisting of perfluoro(alkyl vinyl) ethers, perfluoro(alkoxy vinyl) ethers, and mixtures thereof, and 3) a cure site component containing a halogen group capable of participation in a peroxide cure reaction, selected from the group consisting of fluorinated olefins having at least one such halogen group, fluorinated vinyl ethers having at least one such halogen group, chain transfer agents containing at least one such halogen group, and initiators containing at least one such halogen group, and mixtures thereof; with the proviso that the cure site component contains substantially no nitrile groups, and
  - 15 B) a peroxide curative.
- 20 2. A peroxide curable perfluoroelastomer compound according to Claim 1, wherein the perfluorovinyl ether is selected from the group consisting of perfluoromethyl vinyl ether, perfluoroethyl vinyl ether, and perfluoropropyl vinyl ether.
- 25 3. A peroxide curable perfluoroelastomer compound according to Claim 1, wherein the halogen of the cure site component is bromine or iodine.
- 30 4. A peroxide curable perfluoroelastomer according to Claim 1, wherein the perfluoroelastomer is substantially free of ionizable end groups selected from the group consisting of carboxylate or carboxylic acid end-groups and sulfonate or sulfonic acid end groups.

5. A method for improving the processability of perfluoroelastomers, comprising: polymerizing, under free-radical conditions, an aqueous emulsion or suspension of a polymerizable mixture comprising a perfluoroolefin and a perfluoroalkyl vinyl ether or a perfluoroalkoxy vinyl ether and mixtures thereof, a halogen-containing  
5 cure-site component that is capable of participation in a peroxide cure reaction, a fluoroaliphatic-radical containing sulfinat, and an oxidizing agent capable of oxidizing said sulfinat to a sulfonyl radical, with the proviso that the cure site component contains substantially no nitrile groups.

10 6. A method for improving the processability of perfluoroelastomers, comprising: polymerizing, under free-radical conditions, an aqueous emulsion or suspension of a polymerizable mixture comprising a perfluoroolefin and a perfluoroalkyl vinyl ether or a perfluoroalkoxy vinyl ether and mixtures thereof, a bromine-containing or iodine-containing cure-site component, a fluoroaliphatic-radical containing sulfinat, and  
15 an oxidizing agent capable of oxidizing said sulfinat to a sulfonyl radical.

7. A shaped article comprising the peroxide curable perfluoroelastomer compound of Claim 1.

20 8. A peroxide curable perfluoroelastomer compound according to Claim 7 wherein the perfluoroolefin is tetrafluoroethylene, the perfluoro vinyl ether is perfluoromethyl vinyl ether.

9. A peroxide curable perfluoroelastomer compound according to Claim 1  
25 wherein the cure-site component is said chain transfer agent.

10. A peroxide curable perfluoroelastomer compound according to Claim 1 wherein the cure site component is said chain transfer initiator.

30

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/03490

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C08F214/26

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 02300 A (DU PONT) 23 January 1997 see page 5, line 11 - line 29; claims 1-7; examples 6-21	1,2,4-6, 8
X	FR 2 305 462 A (DU PONT) 22 October 1976 see examples 1,2	1-4
A	US 5 285 002 A (GROOTAERT WERNER M) 8 February 1994 cited in the application see examples	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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FR 2305462 A	22-10-1976	US 4035565 A AU 1239876 A BE 840099 A CA 1076298 A CA 1094247 A DE 2612360 A DE 2659972 C DK 135176 A,B, DK 571777 A,B, GB 1528341 A GB 1528342 A IE 42664 B IE 42665 B JP 925455 C JP 51129481 A JP 53004115 B JP 967146 C JP 52081360 A JP 54001585 B LU 74645 A NL 7603217 A,B NL 7810787 A,B SE 410001 B	12-07-1977 13-10-1977 27-09-1976 22-04-1980 20-01-1981 30-09-1976 11-05-1983 28-09-1976 21-12-1977 11-10-1978 11-10-1978 24-09-1980 24-09-1980 22-09-1978 11-11-1976 14-02-1978 26-07-1979 07-07-1977 26-01-1979 28-01-1977 29-09-1976 30-03-1979 17-09-1979
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(54) Title: PERFLUORINATED ACID FLUORIDES AND PREPARATION THEREOF

(57) Abstract: A method for the preparation of a perfluorinated acid fluoride (especially 3-alkoxy propionic acid fluoride) is pro-  
vided. The method results in high yields of the acid fluoride.

## PERFLUORINATED ACID FLUORIDES AND PREPARATION THEREOF

5

### Field of the Invention

The present invention is related to perfluorinated acid fluorides, especially perfluorinated 3-alkoxy propionic acid fluorides, and a method of preparing such compounds. These compounds are valuable intermediates for e.g. vinyl ethers that can be used to prepare a variety of fluoropolymers including those having enhanced low temperature properties.

10

### Background of the Invention

15

Fluorinated vinyl ethers have found applicability in numerous fluoropolymers. For example, they may be copolymerized with tetrafluoroethylene (TFE) to produce modified polytetrafluoroethylene (mPTFE). Likewise, they may be copolymerized with a variety of other fluorinated monomers to produce fluoroplastic and/or fluoroelastomeric polymers. Some of the benefits of employing vinyl ethers in fluoropolymers are described in various review articles. See for example, Modern Fluoropolymers, John Scheirs, Wiley Series in Polymer Science, 1997. See also Emel'yanov et al, Zh. Org. Khim (1994), 30(8), 1266-70.

20

There are a number of routes to prepare fluorinated vinyl ethers. Generally these routes start with perfluorinated acid fluorides. See for example Modern Fluoropolymers, J. Scheirs, Wiley Series in Polymer Science, 1997 and the literature cited therein.

25

Even though perfluorinated acid fluorides are commonly used in the synthesis of fluorinated vinyl ethers, there are only a few synthetic routes that are known to lead to perfluorinated 3-alkoxy propionic fluorides starting from hydrogen containing precursors.

30

For example, U.S. Patent 2,713,593 discloses the electrochemical fluorination of a nonfluorinated carboxylic acid chloride to form perfluorinated acid fluoride.

Another synthesis route is disclosed in V. V. Berenblit et al., Zh. Prikl. Khim. (Leningrad), (1975) 48(3) 709-11. In this route a hydrocarbon ester is electrochemically fluorinated to provide the perfluorinated acid fluoride.



These synthesis routes are not entirely satisfactory because yield of acid fluoride is low, e.g., less than 15% by weight. This is in keeping with the generally low yields of ethers during electrochemical fluorination.

A third route to the synthesis of acid fluorides is disclosed in EPA 148,482 (Ohisaka et al) and EPA 290,848 (Oka et al). In this route, tetrafluorooxetane is reacted with an at least partially fluorinated acid fluoride. The resulting intermediate is fluorinated to provide a perfluorinated acid fluoride. This synthesis route has at least two disadvantages. First, the tetrafluorooxetane must be synthesized. This adds additional steps, time and cost to the synthesis of the acid fluoride. Second, the reaction of the at least partially fluorinated acid fluoride with the oxetane may result in the formation of oligomers thereby reducing the yield of the desired acid fluoride.

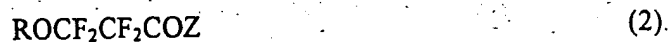
### Summary of the Invention

The present invention provides a process for the preparation of a perfluorinated acid fluoride from a partially fluorinated, hydrogen-containing starting material. The process of the present invention provides a perfluorinated acid fluoride has the formula



wherein  $R_f$  is a perfluorinated linear or branched monovalent aliphatic, preferably alkyl, radical that has from 1-20 (preferably from 1 to 5) carbon atoms. The method of the invention comprises the steps of

- (a) providing a partially fluorinated, hydrogen-containing starting material of the formula



wherein R is a monovalent, hydrogen-containing, linear or branched aliphatic (preferably alkyl) radical that may contain oxygen atoms and that contains from 1-20 (preferably from 1 to 5) carbon atoms; and Z is selected from -OH, a halogen (e.g., chlorine or fluorine) or a monovalent hydrogen-containing linear or branched alkyl or alkoxy group that contains 1-20 (preferably 1-5) carbon atoms, or an anhydride radical selected from  $R'\text{COO}-$  where  $R'$  is selected from R or  $\text{ROCF}_2\text{CF}_2\text{COO}-$  where R is as defined above;

- (b) fluorinating the starting material by contacting it with a fluorinating agent under conditions sufficient to replace hydrogen atoms on the starting material with fluorine; and
- (c) optionally converting the product of step (b) to the perfluorinated acid fluoride.

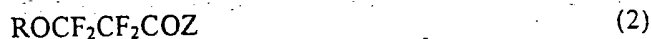
R and Z may be partially fluorinated if desired. Additionally, R and Z may contain one or more oxygen atoms.

As it is used herein, the term perfluorinated means that all of the carbon-bonded hydrogen atoms have been replaced by fluorine.

Surprisingly, the process of the invention provides high yields (preferably 50 mole % or more) of the perfluorinated acid fluoride of the Formula (1). Prior art techniques for producing acid fluorides of formula (1) typically result in yields of the acid fluoride of substantially less than 50 mole %, typically less than 25 mole %. Additionally, the process of the invention is simple to use. It provides the desired acid fluoride in a straight forward manner.

### Detailed Description

The starting material for the process of the invention is the hydrogen-containing compound of the formula



wherein R and Z are as described above. R and Z may be the same or different from one another. Preferably at least one of R and Z is a methyl or ethyl group. The starting materials of Formula (2) are preferably esters, anhydrides or ketones.

When the starting material for the process of the invention is an ester or an anhydride, it has the formula



wherein R'' is a monovalent, hydrogen containing alkyl radical that contains from 1 to 20 (preferably 1 to 5) carbon atoms or

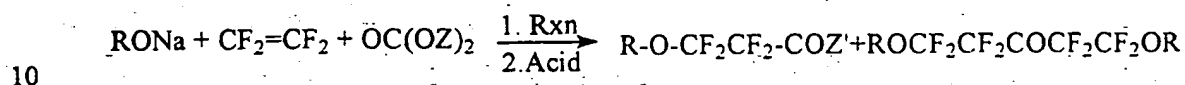


When the starting material is a ketone, it preferably has the formula



where R is as described above.

Starting materials useful in the invention have been previously described. See, for example, U.S. Patent 2,988,537 (Wiley), which disclose the reaction of tetrafluoroethylene (TFE) with a sodium alkoxylate in the presence of a dialkyl carbonate. This reaction  
 5 forms a compound which may then be treated with anhydrous acid to yield a hydrogen-containing, partially fluorinated starting material of Formula (2). This reaction sequence may be graphically represented by the following:



wherein Z' is selected from a halogen, or a monovalent hydrogen containing linear or branched alkyl group of from 1 to 20 carbon atoms, and R is as defined above.

See also U.S. Patent 5,235,094 (Darst et al) which discloses another route to the  
 15 synthesis of a partially fluorinated ester of Formula (3).

The partially fluorinated esters of Formula (3) can be transformed to corresponding anhydrides using procedures well-known to those skilled in the art.

The partially fluorinated starting material is fluorinated by contacting it with  
 20 fluorine to form an intermediate in which all of the hydrogen atoms present on the starting material are replaced with fluorine. This is done under conditions that are appropriate to replace the hydrogen on the starting material, but not so aggressive that backbone of the starting material is disturbed.

Fluorination of the starting material can be accomplished by a number of techniques. Examples of useful fluorination techniques include electrochemical  
 25 fluorination (ECF) and direct fluorination (DF).

Electrochemical fluorination is a well known technique that is disclosed in a number of publications including U.S. Patent 2,713,593 and WO 98/50603. It is a process that employs hydrogen fluoride. Electrochemical fluorination of the starting material results directly in the desired perfluorinated acid fluoride of Formula (1). As a result,  
 30 there is no need to convert the product of this step any further. Surprisingly, the use of the

partially fluorinated precursor of Formula (2) as the starting material results in unexpectedly high yields of the acid fluoride.

Direct fluorination is another well known technique. This technique is disclosed in a host of articles and patents. See for example, U.S. Patent 5,488,142 (Fall et al); U.S. Patent 4,523,039 (Lagow et al); Kirk Othmer Encyclopedia of Chemical Technology, 3<sup>rd</sup> Edition, V. 10, pp 636, 840-855, John Wiley & Sons, Inc., New York, New York (1980); Lagow et al, Progress in Inorganic Chemistry, 26, 161-210 (1979); U.S. Patent 4,859,747 (Bierschenk et al).

During direct fluorination, fluorine, which may be diluted with an inert liquid or gas, and the starting material are contacted in an appropriate vessel (e.g., either a stirred tank reactor or a tubular reactor). The amounts of each are selected to have a stoichiometric excess of fluorine. Fluorination is allowed to take place for a time sufficient to replace all of the hydrogens on the precursor with fluorine.

Direct fluorination of a partially fluorinated starting material is preferably carried out in the presence of an unfluorinated coreactant. The coreactant is often selected from certain common organic solvents. Preferably, the coreactant provides a source of reactive hydrogen that initiates free radical chain reactions between the starting material and the fluorinating agent.

It has been discovered that with the proper selection of the unfluorinated reactant, the yield of the acid fluoride is significantly improved over that otherwise achieved in the practice of the invention. Preferred unfluorinated reactants which provide this surprising enhancement of the yield are non-chlorinated, non-hydroxylic compounds. Most preferably they are ethers. Low molecular weight materials (e.g., weight average molecular weight of 150 or less) are the most preferred.

Examples of unfluorinated reactants that are useful in the practice of the present invention include polar, aprotic compounds and nonpolar, aprotic compounds. Representative examples of polar, aprotic compounds include hydrocarbon esters, acyclic ethers such as diethyl ether, ethylene glycol dimethyl ether, and diethylene glycol dimethyl ether; cyclic ethers such as tetrahydrofuran, 2-methyltetrahydrofuran, dioxane, dioxolane, and 4-methyldioxolane; ketones such as acetone and 2-butanone; carboxylic acid esters such as methyl formate, ethyl formate, methyl acetate, diethyl carbonate, propylene carbonate, ethylene carbonate, and butyrolactones. Mixtures of polar aprotic

compounds may be used if desired. Representative examples of useful nonpolar, aprotic compounds include toluene, benzene, hexane, heptane and the like. Mixtures of nonpolar, aprotic compounds may be used if desired. If desired, polar, aprotic compounds can be mixed with nonpolar, aprotic compounds. Factors involved in the selection include  
5 compatability of the unfluorinated reactants with the starting material to be fluorinated and ease of separation of perfluorinated products.

The unfluorinated coreactants and the partially fluorinated compound of Formula (2) are preferably simultaneously fed to the fluorination vessel. As little as 10% by weight of the coreactant has been found to have a beneficial effect upon yield.

10 Direct fluorination of the starting material results in the formation of a fluorinated intermediate which is then converted to the perfluorinated acid fluoride by techniques known to the art. For example, the intermediate can be converted to the acid fluoride as is described in U.S. Patent 5,466,877 (Moore). Other techniques are, of course, also useful in this conversion.

15 Examples of useful nucleophiles include metal fluorides (e.g., cesium fluoride, potassium fluoride), or tertiary amines (e.g., trialkylamines, pyridine) in an aprotic polar solvent.

As with electrochemical fluorination, direct fluorination of the starting material results in unexpectedly high yields of the acid fluoride.

20 Examples of perfluorinated acid fluorides that may be prepared by the process of the invention include

25  $\text{CF}_3\text{OCF}_2\text{CF}_2\text{COF}$   
 $\text{CF}_3\text{CF}_2\text{OCF}_2\text{CF}_2\text{COF}$   
 $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{COF}$   
 $(\text{CF}_3)_2\text{CFOCF}_2\text{CF}_2\text{COF}$   
 $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{COF}$   
 $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{COF}$   
 $\text{CF}_3\text{OCF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{COF}$

30 As disclosed previously, the acid fluorides prepared by the process of the invention are useful in the preparation of perfluorinated vinyl ethers. These ethers are useful as comonomers in a variety of polymers such as those disclosed in U.S. Patent 4,599,386 (Carlson et al); U.S. Patent 5,115,038 (Ihara et al); U.S. Patent 4,774,304 (Kuhls et al);

U.S. Patent 5,696,616; U.S. Patent 5,639,838; U.S. Patent 4,931,511; U.S. Patent 4,418,186; and U.S. Patent 5,891,965.

### EXAMPLES

#### 5     **Example 1**

A 1000 ml electrochemical fluorination cell similar to the type described in U.S. Pat. No. 2,713,593 (Brice et al.) was equipped with a  $0.037 \text{ m}^2$  ( $0.40 \text{ ft}^2$ ) nickel anode, one  $-40^\circ \text{C}$  and one  $-80^\circ \text{C}$  condenser, both of which convergently drained into a 0.3 L stainless steel decanter. The cell was charged with approximately 900 ml anhydrous HF maintained at 1800 torr (35 psig) and  $58^\circ \text{C}$  while 2224.5 g of a mixture of 90% (wt)  $\text{CH}_3\text{OCF}_2\text{CF}_2\text{CO}_2\text{CH}_3$ , 5%  $(\text{CH}_3\text{OCF}_2)_2\text{C}=\text{O}$  and 5% dimethyl disulfide was added over 218.9 hr. Additional HF was added during the reaction to maintain the fluid level at 900 ml.

Fluorination was carried out as described in Example 1 of WO 98/50603. The cell was operated at an average current of 19.5 amps and an average voltage of 6.0 volts. After the cell had reached steady-state, the current was periodically and regularly interrupted. The current flowed at a first current of 19.5 amps for a first time ( $T_e$ ) of 80 seconds. The current flow was then stopped for a second time ( $T_i$ ) of 4 seconds.

The crude liquid fluorinated product was collected periodically from the decanter for a total of 2384.6 g. In addition, the HF phase in the decanter (total 618.3 g) was found to contain 25 mole % w/w product. The total yield of  $\text{CF}_3\text{OCF}_2\text{CF}_2\text{C}(\text{O})\text{F}$  was approximately 55 mole % of theoretical as determined by GC/IR, GC/MS and  $^{19}\text{F}/^1\text{H}$  NMR. Additionally, the byproduct  $\text{CHF}_2\text{OCF}_2\text{CF}_2\text{C}(\text{O})\text{F}$  was produced in approximately 15 mole % yield.

When this example was repeated using the hydrocarbon ester (that is it was not partially fluorinated) as the starting material, the total yield of the acid fluoride was 21 mole %.

#### **Example 2**

Using a tubular direct fluorination apparatus similar to the type described by Fall and Guerra in U.S. 5,488,142, 108.9 g of 90% (w/w)  $\text{CH}_3\text{OC}_2\text{F}_4\text{COOCH}_3$  - 10% THF was added at 10 ml/hr to a rapidly circulating batch of 5472.7 g perfluoro(N-

methyldimorpholine) to which a gas stream comprised of 400 ml/min  $F_2$  and 1600 ml/min  $N_2$  was continuously introduced. The temperature was maintained at 20° C during the 9.3 hr reaction. Analysis of the crude product by  $^{19}F/^1H$  NMR indicated that the yield of the perfluorinated ester was 75 mole % based on the starting material. The perfluorinated ester was converted to the acid fluoride by contacting the ester with a catalytic amount of pyridine. When this example was repeated without using the THF, the yield was 51 mole %.

When this example was repeated using the hydrocarbon ester (that is it was not partially fluorinated) as the starting material, the total yield of the acid fluoride was 31 mole %.

### Example 3

A 1000 ml electrochemical fluorination cell similar to the type described in U.S. Pat. No. 2,713,593 (Brice et al.) was equipped with a 0.037 m<sup>2</sup> (0.40 ft<sup>2</sup>) nickel anode, one -40° C and one -80° C condenser, both of which convergently drained into a 0.3 L stainless steel decanter. The cell was charged with approximately 900 ml anhydrous HF maintained at 1800 torr (35 psig) and 58° C while 977.9 g of a mixture of 95% (wt)  $CH_3OCF_2CF_2C(O)CF_2CF_2OCH_3$  and 5% dimethyl disulfide was added over 93.0 hr. Additional HF was added during the reaction to maintain the fluid level at 900 ml.

Fluorination was carried out as described in WO 98/50603 using procedures similar to those of Example 1. The cell was operated at an average current of 19.5 amps and an average voltage of 6.1 volts. After the cell had reached steady-state, the current was periodically and regularly interrupted. The current flowed at a first current of 17.8 amps for a first time ( $T_e$ ) of 80 seconds. The current flow was then stopped for a second time ( $T_i$ ) of 4 seconds.

The crude liquid fluorinated product was collected periodically from the decanter, for a total of 1269.9 g. In addition, the HF phase in the decanter (total 364.1 g) was found to contain 2 mole % w/w product. The total yield of  $CF_3OCF_2CF_2C(O)F$  was approximately 50 mole % of theoretical as determined by GC/IR, GC/MS and  $^{19}F/^1H$  NMR.

### Example 4

The partially fluorinated anhydride  $(\text{CH}_3\text{OC}_2\text{F}_4\text{CO})_2\text{O}$  was prepared from  $\text{CH}_3\text{OC}_2\text{F}_4\text{COOCH}_3$ . The ester (83 g, 0.438 mol)  $\text{CH}_3\text{OC}_2\text{F}_4\text{COOCH}_3$  was titrated with aqueous NaOH and MeOH was removed. Concentrated aqueous HCl was added to give 68 g  $\text{CH}_3\text{OC}_2\text{F}_4\text{COOH}$ , bp 76-78° C/15 mm for an 88% yield. A sample of 48 g sample of  $\text{CH}_3\text{OC}_2\text{F}_4\text{COOH}$  was dehydrated with  $\text{P}_2\text{O}_5$  to give 36 g  $(\text{CH}_3\text{OC}_2\text{F}_4\text{CO})_2\text{O}$ , bp 72-76° C/15 mm. The resulting partially fluorinated compound was then directly fluorinated using a tubular direct fluorination apparatus similar to the type described by Fall and Guerrain U.S. 5,488,142. Direct fluorination of 19.6 g of  $(\text{CH}_3\text{OC}_2\text{F}_4\text{CO})_2\text{O}$  in perfluoro(N-methylmorpholine) at 25° C with 10% THF as a cosolvent gave 14.5 g  $(\text{CF}_3\text{OC}_2\text{F}_4\text{CO})_2\text{O}$  identified by  $^{19}\text{F}$  NMR in a 56% yield. The perfluorinated anhydride can be converted to the acid fluoride using known techniques. For example, it can be reacted with KF to form a mixture of the acid fluoride and the corresponding potassium salt. The salt can then be converted to the acid fluoride in a subsequent reaction. Alternatively, the anhydride can be reacted with HF to provide the acid fluoride by contacting the anhydride with a catalytic amount of pyridine.



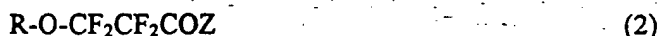
## CLAIMS

1. A method of making a perfluorinated acid fluoride having the formula-



5 wherein  $R_f$  is a perfluoroaliphatic group having from 1 to 20 carbon atoms, comprising the steps of

- (a) providing a partially fluorinated, hydrogen-containing starting material of the formula



10 wherein R is a monovalent hydrogen-containing aliphatic group that may contain one or more oxygen atoms and that has from 1 to 20 carbon atoms and Z is selected from -OH, a halogen or a monovalent, hydrogen-containing linear or branched alkyl or alkoxy group from 1 to 20 carbon atoms, and an anhydride radical selected from R'COO- where R' is selected from R or  $ROCF_2 CF_2 COO-$ , and

- 15 (b) fluorinating the starting material by contacting the starting material with a fluorinating agent under conditions sufficient to replace the hydrogen atoms on the starting material with fluorine; and  
20 (c) optionally converting the product of step b) to the perfluorinated acid fluoride.

2. The method of claim 1 wherein at least one of R and Z are partially fluorinated.

25 3. The method of claim 1 wherein R and Z are free from fluorine.

4. The method of claim 1 wherein each R and Z independently have from 1 to 5 carbon atoms.

30 5. The method of claim 1 wherein at least one of R contains a methyl or ethyl group and Z contains a methoxy or an ethoxy group.

6. The method of claim 1 wherein Z is a halogen.

7. The method of claim 1 wherein step (b) is done by electrochemical fluorination.

8. The method of claim 1 wherein step (b) is done by direct fluorination.

9. The method of claim 1 wherein the starting material has the formula



wherein R is a linear or branched, hydrogen-containing aliphatic group having from 1 to 20 carbon atoms, R'' is a monovalent, hydrogen-containing alkyl or alkoxy radical that contains from 1 to 20 carbon atoms or



10. The method of claim 9 wherein R and R'' are partially fluorinated.

11. The method of claim 9 wherein R and R'' are free from fluorine.

12. The method of claim 9 wherein each R and R'' independently have from 1 to 5 carbon atoms.

13. The method of claim 9 wherein at least one of R and R'' is methyl or ethyl.

14. The method of claim 9 wherein R is an alkyl group.

15. The method of claim 1 wherein the starting material has the formula



wherein R is a linear or branched, hydrogen-containing aliphatic group having from 1 to 20 carbon atoms.

16. A method of making a perfluorinated acid fluoride having the formula



wherein  $R_f$  is an aliphatic group having from 1 to 20 carbon atoms comprising the steps of

- (a) providing a partially fluorinated, hydrogen-containing starting material of the formula



wherein R is a monovalent hydrogen-containing aliphatic group having from 1 to 20 carbon atoms and Z is selected from -OH, a halogen or a monovalent, hydrogen-containing linear or branched alkyl or alkoxy group containing from 1 to 20 carbon atoms, and an anhydride radical selected from  $R'COO-$  where  $R'$  is selected from R or  $ROCF_2 CF_2 COO-$ ; and

- (b) combining the starting material and an unfluorinated coreactant in a suitable vessel;
- (c) fluorinating the starting material in the combination from step (b) by direct fluorination; and
- (d) converting the fluorinated product of step (c) to the perfluorinated acid fluoride.

17. The method of claim 18 wherein the combination of step (b) comprises from at least 10% by weight of the unfluorinated coreactant.

18. The method of claim 17 wherein the unfluorinated coreactant is a low-molecular weight non-chlorinated, non-hydroxylic compound.

19. The method of claim 17 wherein the unfluorinated coreactant is an ether.

20. The method of claim 17 wherein the unfluorinated coreactant is a hydrocarbon ester.

# INTERNATIONAL SEARCH REPORT

International Application No:  
PCT/US 00/10812

A. CLASSIFICATION OF SUBJECT MATTER  
C07C59/315, C07C51/363

According to International Patent Classification (IPC) or to both national classification and IPC<sup>7</sup>

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2713593 A (BRICE, T. J. et al.) 19 July 1955, the whole document (cited in the application).	1, 8, 9, 16
A	US 5093432 A (BIERSCHENK et al.) 03 March 1992, claims, column 5, line 6 - column 7, line 13.	1, 15, 16
A	PATENT ABSTRACTS OF JAPAN vol. 9, no. 32 (C-265), 09 February 1985 & JP 59 177384 A (ASAHI KASEI KOGYO K.K.) 08 October 1984, abstract.	1, 7, 9, 16

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

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## INTERNATIONAL SEARCH REPORT

- 2 -

PCT/US 00/10812

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	-- EP 0354420 A (HOECHST AKTIENGESELLSCHAFT) 14 February 1990, the whole document.	1, 15, 16
A	-- CHEMICAL ABSTRACTS, vol. 83, no. 23, 08 December 1975 Columbus, Ohio, US; abstract no. 192495y, ADCOCK, J.L. et al.: 'Successful direct fluorination of oxygen-containing hydrocarbons' page 389, column 2; & J. Org. Chem., vol. 40, no. 22, 1975, pages 3271-3275, abstract.	1, 8, 9, 16
A	-- US 5466877 A (MOORE) 14 November 1995, claims (cited in the application).	1, 8, 9, 16-19
A	-- US 5488142 A (FALL et al.) 30 January 1996, claims (cited in the application). ----	1, 8, 15-20

ANHANG		ANNEX		ANNEXE			
Zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.		To the International Search Report to the international Patent Application No.		Au rapport de recherche international relatif à la demande de brevet international n°			
In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentedokumente angegeben. Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.		This annex lists the patent family members relating to the patent documents cited in the above-mentioned search report. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.		La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visée ci-dessus. Les renseignements fournis sont donnés à titre indicatif et n'engagent pas la responsabilité de l' Office.			
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				EP B1 646557		13-08-1997	
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